Quanlin Zhou Research Summary

During my stay at LBNL from 2001, I have been working on (1) the DOE's Yucca Mountain Project for characterizing Yucca Mountain, Nevada, as the first geologic repository site for high-level nuclear waste disposal, (2) the DOE's geologic carbon sequestration projects for mitigating global climate change, and (3) site-specific contamination remediation and assessment projects.

For the Yucca Mountain Project, I focused my research on:

- Scale dependence of the field-scale, effective matrix diffusion coefficient in fractured media, enhanced retardation of solute/radionuclide transport by diffusive mass transfer between fractures and the matrix in heterogeneous fractured rock, and scale dependence of the mass transfer coefficient in porous media [J8, J10, J11, J12, and J13];
- Effects of flow focusing in unsaturated, heterogeneous fractured rock on total system performance assessment, and calibration of unsaturated zone properties [C15];
- Pretest prediction and analysis of the Alcove 8–Niche 3 field infiltration/seepage and tracer tests (conducted at mesoscale in two tunnels), and understanding of observed spatial variability of infiltration/seepage rates and mapped fracture patterns [J14];
- Effects of multiscale heterogeneity in fracture/matrix permeability and capillarity on unsaturated flow and radionuclide transport—by characterizing and calibrating the spatial variability of fracture and matrix properties at multiple scales [J17].

For the geologic carbon sequestration (GCS) projects funded by DOE's National Energy Technology Laboratory and EPA, I have been focusing and will focus my research on the framework of risk assessment and management (for both CO₂ plume scale and sedimentary basin scale):

- Geologic storage and groundwater resources: large-scale hydrogeological evaluation and impact on groundwater systems, including pressure propagation to shallow aquifers and native brine displacement, and site-specific evaluation of the large-scale impact in the Illinois Basin, IL, and the San Joaquin Basin (Kimberlina site), CA, where DOE's Phase III demonstration projects are under way [J5, J6, J7];
- CO₂ plume scale: Enhanced storage capacity and safety (with reduced CO₂ leakage risk) in hierarchical, multiscale, heterogeneous sedimentary rock, and CO₂ trapping by (1) capillary intrusion and diffusive transport of (dissolved CO₂) into numerous low-permeability shale lenses from viscous, mobile CO₂ fingers in sand channels and (2) density-driven fingering of dissolved CO₂, enhanced by the natural hierarchical, sedimentary architecture and multiscale heterogeneity [J1, J2];
- Sedimentary basin scale: Dynamic pressure buildup in storage formations and overlying units, natural attenuation and mitigation of pressure through imperfect sealing units, and imperfections (e.g., abandoned wells and undetected fault zones); the natural attenuation and mitigation of pressure in response to CO₂ injection and storage during the full-scale deployment is critical to the effectiveness of GCS for climate-change mitigation, in terms of storage capacity [J1].

- Early warning and detection of CO₂ leakage based on real-time pressure monitoring and inverse modeling, use of far-field pressure monitoring data to detect brine leakage through imperfections, and to further predict CO₂ leakage when CO₂ is continuously injected, leading to the plume arrival at the imperfections.
- Evaluation of the EPA Area-of-Review and leakage through abandoned wells using integrated analytical solutions for multilayered sedimentary basins for pressure buildup, brine displacement, and CO₂ plume. A new collaborative work with EPA was initiated and fund has been secured [J5].

I have been involved in four individual projects related to site-specific contamination remediation and assessment. Through detailed data analysis and model calibration, I have been devoted to physically based remediation measures and in-situ biodegradation evidenced from detailed monitoring data. Specifically, I have focused my research on:

- Development and calibration of a three-dimensional numerical model for modeling groundwater flow and advective transport at the DNAPL-contaminated LBNL site in support of the ongoing remediation process: hydraulic control of dissolved DNAPL plumes [J16];
- Photo- and biodegradation of N-nitrosodimethylamine (NDMA) in a coupled surface water and groundwater system with active recycled water recharge in Montebello Forebay, Los Angeles, California. Evidence of in-situ biodegradation in saturated groundwater was, for the first time, obtained through detailed monitoring, data analysis, and modeling. This research is of significance to water supply in the Los Angeles Metropolitan with expanded artificial recharge [J3, J4, C8, C11, C12];
- Transport of tritium in the NuMI underground facility at FermiLab, IL, where tritium was
 generated in concrete shielding, fractured rock, steel, and vapor by accelerator experiments. Key
 components and processes are global transport of tritiated water vapor through the tunnel,
 diffusive deposition into unsaturated concrete and rock in contact with the tunnel, and diffusive
 tritium transport within concrete and steel. This is an excellent case for investigation of
 multiphase diffusive transport phenomena [a series of journal publications are under
 preparation];
- Modeling of DNAPL migration and dissolved component transport in a weathered, fractured rock zone at a contaminated site in Charlotte, North Carolina, in support of full-scale remediation; evidence of back diffusion from the matrix to fractures in response to remediation of a long-term TCE plume.

In 2000, my postdoctoral research at MIT was on multiphase flow simulation and effects of heterogeneity on multiphase flow (effective properties and DNAPL lateral spreading). The effective properties of multiphase flow obtained by numerical simulation were compared with those obtained by spectral-perturbation analysis, and a reasonable agreement was obtained. My PhD research (1996–1999) at Technion was on modeling seawater intrusion in coastal aquifers, with applications to seawater intrusion in the coastal aquifer of Israel. In China (1990–1996), I was engaged in research on surface water modeling, water resources systems analysis, and risk and uncertainty analysis.

During the time I have served on projects related to DOE's missions for geologic waste disposal and containment and remediation, I have developed my scientific research capabilities in three major categories: (1) diffusive transport phenomena in fractured and porous media at field scale, (2) flow and transport in heterogeneous fractured/porous media in single- and multiphase conditions, and (3) analytic and numerical modeling of geologic carbon sequestration.

Diffusive Transport Phenomena in Fractured and Porous Media [J8, J10, J11, J12, J13]

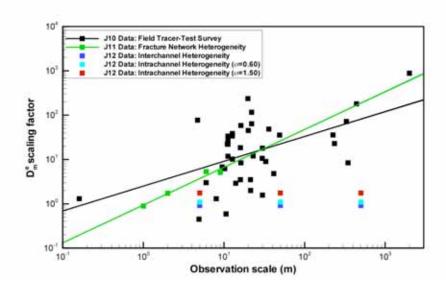
Since matrix diffusion was employed to interpret a groundwater tritium anomaly observed in the field [Foster, 1975], diffusive transport has been demonstrated to be one of the key transport phenomena in fractured rock, as reflected in mathematical modeling, laboratory experiments, and field tracer tests. For heterogeneous fractured rock and porous media, two different types of scale-dependence behavior for the field-scale, effective matrix diffusion coefficient or mass-transfer rate coefficient have been suggested, following the findings of scale-dependent hydraulic conductivity and macrodispersivity.

The first scaling behavior, proposed by our research group, is that the field-scale, effective matrix diffusion coefficient (D_m^e) increases with observation scale (L), a transport mechanism for enhanced retardation of solute/radionuclide in fractured rock. The scaling factor (F_D) of the effective matrix diffusion coefficient is defined as the ratio of D_m^e to the geometric mean (D_m^G) of local-scale matrix diffusion coefficient (D_m) , and the scaling slope of $\log_{10}(F_D)$ as a function of $\log_{10}(L)$ is used to describe this scaling behavior. To confirm the proposed scale dependence of effective matrix diffusion coefficient, we have conducted (1) a comprehensive and critical literature survey, (2) numerical experiments, and (3) field tracer test analyses, as summarized in my Journal Publications J10 through J13 in the above list:

- J10. We have conducted a critical review of all field-scale tracer tests available in the literature, selected 40 field tracer tests from 15 geologic sites, reanalyzed some of the tracer tests, and concluded that the field-scale, effective matrix diffusion coefficient is scale-dependent. The field-scale, effective matrix diffusion coefficient varies from 0.5 to 884 for the observation scale ranging from 5 to 2,000 m, with a scaling slope of 0.66. The tracer-test reanalysis was conducted using various (semi-) analytic solutions implemented in the iTOUGH2-TRAT code for inverse modeling. We also demonstrated that the field-scale dispersivity in fractured rock is scale dependent in the framework of advection-dispersion-diffusion calibration, consistent with previous findings by Gelhar and others. Various mechanisms behind the scale-dependence behavior and enhancement of matrix diffusion were suggested.
- J11. One mechanism is the network of multiscale (length, aperture) fractures. We conducted numerical experiments to investigate the contribution of heterogeneity in fracture network to the observed scale dependence behavior. A combination of local, multilevel flow loops (in relatively small fractures) and a global flow path (in a backbone fracture), with some scaling features of network geometry, was used to represent a complex multiscale fracture network. Matrix diffusion was employed to represent mass transfer between fractures and the matrix. The effective diffusion coefficient was calibrated for different locations along the global flow path. Experimental results indicate that the effective matrix diffusion coefficient increases with observation scale, with a slope dependent on the local matrix diffusion coefficient, aperture ratios between different levels

- of fractures, and the scaling feature for the fracture network. The scaling slope can be as high as 1.0 when all favorable conditions prevail along a travel distance less than 10 m. In these numerical experiments, a constant local matrix diffusion coefficient was used. In summary, the geometry of a multiscale fracture network with the ultimate process of matrix diffusion is the key for the scale-dependent behavior of field-scale, effective matrix diffusion coefficient.
- J12. The other mechanism is the spatial variability of the local-scale matrix diffusion coefficient (D_m) along the flow path within a single fracture (i.e., intrachannel heterogeneity) and among different fracture channels (i.e., interchannel heterogeneity). Numerical experiments were conducted for a fracture network of 10 separate, parallel channels, with lognormal distribution of the local matrix diffusion coefficient and water mixing only at the observation points (e.g., pumping wells) a 5, 50, and 500 m. No scale dependence of the calibrated matrix diffusion coefficient was observed, nor was any enhancement of matrix diffusion (calibrated D_m^e versus D_m^G , the geometric mean of D_m) for the interchannel heterogeneity. In the numerical experiments with intrachannel heterogeneity, it was observed that $D_m^e > D_m^G$, indicating an enhancement in matrix diffusion. An empirical estimate of D_m^e was given as a function of the variance of $\ln(D_m)$. However, no scale dependence was observed for the random fields of $ln(D_m)$ (with negligible correlation length) used in this paper. Only when the ratio between the integral scale of $ln(D_m)$, and the observation scale was between 0.1 and 10, could the scale dependence caused by intrachannel heterogeneity along the single-fracture flow path occur, as demonstrated by stochastic analysis in Dai et al. [2007]. However, the scaling slope for the observed scale dependence caused solely by the heterogeneity in the local matrix diffusion coefficient is very small, with the maximum scaling factor being 1.44 for 1,000 m.
- J13. The other type of heterogeneity is the spatial variability of the local-scale matrix diffusion coefficient within the rock matrix in the direction perpendicular to the fracture-matrix wall. To analyze the effect of this type of heterogeneity, a unique, field-scale tracer test over 600 days, with 350 days of constant-rate injection, was reanalyzed with the detailed fracture and matrix data available. Three different diffusion processes—(1) diffusion into stagnant water and infilling materials within fractures, (2) diffusion into a degraded matrix zone, and (3) further diffusion into an intact matrix zone—were evidenced from the steep rising limb, slow increasing platform, and decay-like falling limb of the concentration breakthrough curve. Different matrix diffusion coefficients were calibrated for the three zones. Short-term and long-term effects of these diffusion zones were also investigated, indicating that the thin degraded zone and within-fracture stagnant water and infilling material are critical to analysis of field-tracer tests, but their impact on long-term transport is negligible in comparison with the thick intact matrix zone.

These four publications present our understanding of the scale-dependent, field-scale effective matrix diffusion coefficient for fractured rocks (see the following Figure), complementing the understanding of other mechanisms for enhancement and scale-dependence behavior within field-scale diffusive transport (published by Neretnieks and his group, among many others, in the literature).



The second scaling behavior is shown by the mass transfer rate coefficient in porous media decreasing with experimental duration or residence time, evidenced from the analyses of numerous transport experiments by Haggerty et al. [2004]. Three causes for this scale-dependence behavior have been presented in the literature: (1) inseparable advective and diffusive transport between low-conductivity immobile and high-conductivity mobile zones, (2) inadequate characterization of the first-order mass-transfer model, and (3) multirate diffusion caused by sub-REV-scale heterogeneity. Based on 316 experiments (predominantly with the first-order model parameter available only), Haggerty et al. [2004] showed that the effective mass-transfer rate coefficient is much better correlated to the experimental/observational duration and solute residence time than velocity, and concluded that multirate diffusion might be a key cause for the scale behavior, in addition to the other two causes.

Our observations challenged Haggerty et al.'s [2004] conclusion in the following three ways:

J8. We employed the MADE-2 field tracer test, a natural gradient tracer (tritium) test, to examine the scale behavior of the mass-transfer rate coefficient, using the dual-porosity model in a threedimensional flow and transport model. Hydraulic conductivity at mesh nodes was interpolated using a fractional Brownian motion model with detailed conductivity measurements. The mass-transfer rate coefficient was calibrated for each of the four plume snapshots at 27, 132, 224, and 328 days to obtain reasonable match between simulated and measured total mass in mobile regions and mass center locations. The calibrated mass transfer coefficient decreases from 0.5 day⁻¹ at 27 and 132 days, to 0.002 day⁻¹ at 224 days, and further to 0.0005 day⁻¹ at 328 days, over three orders of magnitude. This observed scale-dependence behavior is similar to that of Haggerty et al. [2004], as well as others. However, unlike Haggerty et al. [2004], we interpreted the observed scaledependence using an analytical solution for a layered system with the MADE-site-specific thickness of low- and high-conductivity zones. A constant single-rate diffusion coefficient value was used. The precisely calculated mass-transfer coefficient also decreases with time by two orders of magnitude. We concluded that the first-order mass-transfer model used in the dual-porosity model cannot capture transient concentration gradients at the interfaces between high- and lowconductivity zones, and requires a time-dependent mass-transfer coefficient to reproduce the

- transport processes. This scale-dependence behavior does not result from any heterogeneity or physical processes, but is an artifact of numerical approximations.
- J10. We investigated the correlation between the calibrated effective matrix diffusion coefficient and experiment duration, as well as velocity, and found no correlations for the 40 tracer tests in our literature survey. This can be attributed to the contrast of hydraulic conductivity between fractures and the rock matrix being higher than four orders of magnitude, by excluding all field tracer tests in fractured porous media with smaller contrasts. Advective transport between fractures and the matrix is not the case here.
- J12. No correlation between velocity and effective matrix diffusion coefficient was also found in this paper for fractured rock. More importantly, the scaling effect caused by multirate diffusion with interchannel and intrachannel heterogeneity was demonstrated to be very minor, if any, in comparison with that caused by heterogeneous fracture network.

Through our five journal publications, we demonstrated that the field-scale, effective matrix diffusion coefficient for fractured rock is scale dependent, using a critical literature review, numerical experiments, and tracer-test analyses. This behavior stems from the heterogeneous network of multiscale fractures, rather than the spatial variability in the local-scale matrix diffusion coefficient. Following the analyses of numerous experiments using the first-order mass-transfer model, we analyzed the MADE-2 tracer test and concluded that the field-scale mass-transfer rate coefficient decreases over tracer residence time. However, we challenged Haggerty et al.'s [2004] conclusion, in that this scale-dependent behavior is mainly an artifact of numerical model approximations, rather than the real physical process of multirate diffusion.

Flow and Transport in Heterogeneous Fractured/Porous Media [J14, J16, J17]

In addition to my research on the scale dependence of field-scale, effective matrix diffusion coefficient in fractured rock caused by various types of heterogeneity, I have also focused on a broader research area in flow and transport in heterogeneous fractured/porous media, through (1) characterization of multiscale heterogeneity in the hydrogeologic properties of the fractured unsaturated zone, (2) analysis of a mesoscale infiltration and seepage test and correlation between infiltration/seepage rates and mapped fractured patterns, and (3) calibration of saturated groundwater flow at a DNAPL-contaminated site in support of onsite remediation.

J17. Characterization of multiscale heterogeneity in unsaturated fractured rock, and analysis of its impact on unsaturated flow and transport are important to the total system performance assessment of any geologic sites. We developed a conceptual model for the unsaturated zone of fractured rock at Yucca Mountain to represent complex heterogeneity at two scales: (1) layer scale, corresponding to geologic layering, and (2) local scale, for intralayer spatial variabilities. The layer-scale hydrogeologic properties were calibrated based on available measurements of water saturation and potential in the matrix, and pneumatic pressure in boreholes. The intralayer variabilities (by mean, variance, and correlation length) were characterized using data for each hydrogeologic layer. Random fields of matrix permeability, matrix van Genuchten α, and fracture permeability were generated, and the unsaturated flow and transport of a conservative tracer was simulated. Results show that local-scale heterogeneity has a considerable effect on unsaturated flow processes, leading to fast flow paths in both fractures and the matrix. As a result, a noticeable effect on global tracer transport is observed: early arrival of tracer mass.

- J14. Field infiltration/seepage tests are critical to bridging our knowledge gap between transport processes at small scale and large-scale processes in complex fractured rock, and to gain of our confidence in site-scale modeling capabilities and results. A mesoscale infiltration and seepage test was conducted in a deep unsaturated fractured rock system by infiltration under ponded conditions in the upper-tunnel alcove and by collecting seepage at the lower-tunnel niche at Yucca Mountain. Spatial variabilities of infiltration and seepage rates were measured using multiple infiltration subplots and seepage trays. A three-dimensional unsaturated flow model was developed to reproduce the strong temporal and spatial variabilities in infiltration and seepage rates observed. Calibrated fracture permeability and van Genuchten α represent their respective spatial variabilities reflected in infiltration/seepage variabilities. The measured infiltration rates were found to be partially controlled by the fracture patterns on the infiltration plot, whereas no correlation was established between measured seepage rates and the density of fractures mapped on the niche ceiling. More importantly, numerous small fractures excluded in fracture mapping complicate such correlations, and the complexity of preferential unsaturated flow within the discrete fracture network can be attributed to the lack of correlation. The pervasive small fractures may be the key factor in the scale dependence of the effective matrix diffusion coefficient, as discussed above.
- J5. Modeling and calibration of all processes relevant to on-site remediation are useful decision-support tools, particularly with respect to natural heterogeneity. A three-dimensional groundwater flow and advective transport model was developed at a heterogeneous, mountaineous site contaminated by DNAPL—in support of on-site remediation. The observed flow and plume conditions reflect the spatial variability in hydraulic conductivity and effective porosity. Calibration of these properties in several property zones was conducted. The calibrated effective porosity turns out to be much lower than the core porosity, indicating that only a small fraction of all pores are connected in the rock media. The calibrated flow properties combined with the measured boundary conditions can accurately reproduce the evolution of the dissolved DNAPL plume.

My additional research in this area includes the effects of heterogeneity on multiphase (DNAPL and water) flow, including the enhanced anisotropy of relative permeability by longer correlation length in the horizontal direction, and lateral spreading of DNAPL. This research will be extended to investigation of viscous fingering of phase CO₂ in hierarchical, multiscale, heterogeneous sedimentary sandstones for geologic carbon sequestration.

Analytic and Numerical Modeling of Geologic Carbon Sequestration [J1, J2, J5, J6, J7]

Geologic carbon sequestration (GCS) potentially is an effective measure for mitigating climate change. Its effectiveness depends on the storage capacity of sedimentary basins versus cumulative CO₂ emission, and the environmental impact of GCS (e.g., CO₂ leakage). I have been working on GCS for three years, focusing my research on the large-scale impact of CO₂ storage on groundwater resources in shallow aquifers, including pressure propagation and brine displacement. Meanwhile, I am developing research in (1) enhanced storage capacity and safety in hierarchical, multiscale heterogeneous sedimentary rock (with the aid of our experience in low oil recovery of reservoir engineering), and (2) early warning of CO₂ leakage through sealing unit imperfections (e.g., fractures, abandoned wells, and fault zones) by real-time pressure monitoring, understanding pressure behavior, and inverse modeling, and (3) a framework of risk assessment and management at both CO₂ plume scale and sedimentary basin scale in support EPA regulation.

My five journal publications (on carbon sequestration) present my research on pressure propagation and brine displacement at large scales, from the storage formation to the shallowest freshwater aquifer. Numerical modeling of multiphase flow (CO₂, water, and NaCl) and multicomponent transport is the key instrument for our understanding. Analytic solutions are also developed for a laterally bounded aquifer-aquitard system, complementing the solutions for infinite systems developed by Theis, Hantush, Neuman, and Moench. A storage scenario for full-scale deployment of GCS in the Illinois Basin, as an example, has been studied to answer how much we can store CO₂ underground considering pressure-related caprock integrity and environmental constraints.

- J1. As an example, an integrated modeling of basin- and plume-scale transport processes for a scenario of full-scale deployment of GCS in the Illinois Basin was conducted, on the basis of detailed site characterization. Twenty storage sites, located in the central most suitable area, referred to as core injection area, of 24,000 km², were employed with annual injection rate of 5 million metric tonnes CO₂ per site over 50 years. The storage rate accounts for one third of the current CO2 emissions in the region. Significant pressure buildup (as high as 35 bar) was observed in the core injection area and moderate pressure buildup is propagated to the margin of the Illinois Basin of 240,000 km2. There are various conditions in the selected core injection area favorable to the large-scale deployment of GCS, as shown by the plume-scale CO2 behavior.
- J2. On the basis of the integrated modeling of GCS the Illinois Basin, the implications of the model results to storage capacity assessment and GCS regulation were discussed. Any storage capacity assessment has to base on detailed modeling with site-specific pore compressibility and preliminarily designed storage scenario for the ultimate deployment; the methodology based on pore space available may overestimate storage capacity, in particular for low pore compressibility sandstones.
- J5. We developed semi-analytical solutions to address the injection/storage-induced pressure perturbation and vertical leakage in a "laterally bounded" system. A one-dimensional radial-flow equation for the aquifer was coupled with a one-dimensional vertical-flow equation for the aquitards. Analytical solutions in the Laplace-transform domain were obtained for (1) pressure change in the aquifer and in the underlying/overlying aquitards, (2) rate and volume of leakage through the aquifer-aquitard interface integrated up to an arbitrary radial distance, (3) total leakage rate and volume for the entire interface, and (4) integrated horizontal flux at an arbitrary radius. The derived analytic solutions for bounded systems are the generalized solutions of infinite systems, with an extra term reflecting the effect of the no-flow boundary. In addition, it was mathematically proven that the total leakage rate and volume are independent of the aquifer's radial extent and wellbore radius, a scale invariant, self-adjusting phenomenon. Laplace-transform solutions were numerically inverted to obtain the pressure change, leakage rate, and leakage volume for the given hydrogeologic and geometric conditions of the aquifer-aquitard system.
- J6. Large volumes of CO₂ captured from carbon emitters such as coal-fired power plants may be stored in deep saline aquifers as a means of mitigating climate change. Storing these additional fluids may cause pressure changes and displacement of native brines, affecting subsurface volumes that can be significantly larger than the CO₂ plume itself. Serious environmental impacts on groundwater resources may result if the deep parts of the basin communicate effectively with shallow units. One concern is the large-scale pressure perturbation within a storage formation that may extend updip to a shallow freshwater aquifer or recharge/discharge zones. Another would be the slow pressure propagation in the vertical direction, limited but possibly not inhibited by the sealing formations that

separate deep and shallow units. In an attempt to address these issues quantitatively, we have conducted numerical simulations that provide a basic understanding of the large-scale flow and pressure conditions in response to industrial-scale CO₂ injection into a laterally open saline aquifer. The model domain includes an idealized multilayer groundwater system, with a sequence of aquifers and aquitards (sealing layers) extending from the deep saline storage formation to the top of the uppermost aquifer. Simulation results show the region of influence during/after injection of CO₂ in both lateral and vertical directions. For seal permeability higher than 0.01 mDarcy, pressure buildup of at least 1.0 m occurs in the shallow groundwater aquifer. With seal permeability of 0.001 mDarcy (representative of a number of CO₂ storage or test sites), interlayer communication through low-permeability seals significantly reduces the pressure buildup in the storage formation, avoiding geomechanical damage of the sealing units.

J7. Carbon dioxide may be stored in compartmentalized closed and semi-closed systems with no-flow radial boundaries, with the benefit of low CO₂ leakage risks. However, the pressure buildup caused by continuous industrial-scale CO₂ injection may have a limiting effect on CO₂ storage capacity. The storage capacity and pressure buildup in these systems were investigated using numerical simulations. An analytic solution was developed for the quick assessment of the CO₂ storage capacity. This quick-assessment method is based on the fact that native brine (of an equivalent volume) displaced by the cumulative injected CO₂ occupies additional pore volume within the storage formation and the seals, provided by pore and brine compressibility in response to pressure buildup. With nonideal seals, brine may also leak through the seals into overlying/underlying formations. The quick-assessment method calculates these brine displacement contributions in response to an estimated average pressure buildup in the storage reservoir. The developed solution can be used as a screening tool for site selection.